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(54) Ethylene polymer blend.

(57) Ethylene polymer blends of a high molecular weight ethylene polymer, preferably an ethylene-mono-1-olefin copolymer, and a low molecular weight ethylene polymer preferably an ethylene homopolymer, both preferably with narrow molecular weight distribution and low levels of long chain branching exhibit excellent film properties and good environmental stress crack behavior superior to that expected for polyethylene of comparable density and melt flow. These resins are useful for the manufacture of film or in blow molding techniques, the production of pipes and wire coating.

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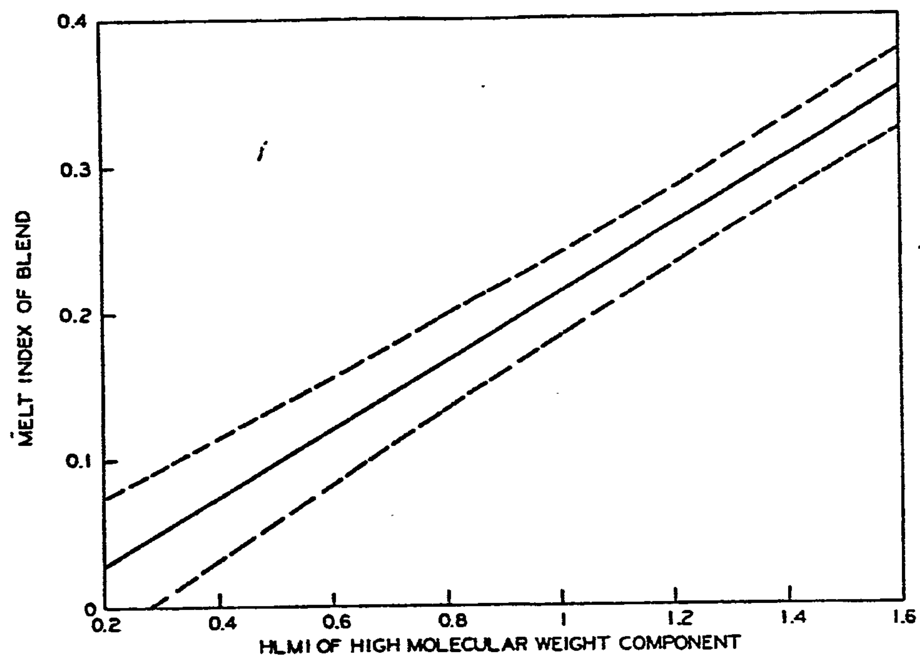

EFFECT OF HLMI OF HIGH MOLECULAR WEIGHT COMPONENT ON MELT INDEX OF BLEND CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 1

ETHYLENE POLYMER BLENDS

Background of the Invention

The present invention relates to the production and use of blends of ethylene polymers of different molecular weight. More specifically the present invention relates to film grade ethylene polymer blends.

In recent years high density polyethylene film has been commercially very successful as a replacement for kraft paper. Several new film resins have therefore been introduced on the market. Among these new resins are high molecular weight high density polyethylene resins having a broad molecular weight distribution.

The production of high density polyethylene today can be called a mature technology. One of the continuing goals in this technology is to develop catalysts with high productivities so that a catalyst removal step can be avoided in the polymer production. Such high productivity catalysts have been developed in recent years. These catalysts sometimes produce ethylene polymers with a narrow molecular weight distribution.

Thus, resins produced with certain high productivity catalysts in view of their narrow molecular weight distribution are often not ideal for the above described application of the high density polyethylene as a film forming resin. It would be very desirable to have an ethylene polymer composition available which can be produced with high productivity catalysts and which still has film grade resin qualities. There is a further specific problem encountered in the production of resins for applications as films. The film properties desired and the desired processability of the resin are often in conflict. Improvements on the

processability frequently result in reduced film qualities and vice versa.

The desired properties of film for many applications conflict with each other. For example, polymers with good toughness (impact resistance) are usually deficient in stiffness for grocery sacks. Those that make stiff sacks are too brittle. Thus, most film polymers are a compromise: a balance of performance features.

The Invention

It is one object of this invention to provide an ethylene polymer resin composition useful for such applications as film production.

Another object of this invention is to provide ethylene polymer resin mixtures that are satisfactory with respect to both the film properties and the processability of the resin.

Another object of this invention is to provide ethylene polymer resin for blown film applications.

A further object of this invention is to provide ethylene polymer resin compositions, the polymers of which can be made with high productivity olefin polymerization catalysts.

Yet another object of this invention is to provide a process for the production of such resin compositions.

Still another object of this invention is to provide a process for the manufacture of polyolefin film from such a resin composition which has acceptable film properties.

A yet further object of this invention is to provide an ethylene polymer film having high strength and, in particular, high tear strength, puncture resistance, impact strength and high environmental stress crack resistance (ESCR).

An important object of this invention is to provide a resin composition having a better balance of stiffness and impact and ESCR as compared to known resins.

These and other objects, advantages, features, details and embodiments of this invention will become apparent to those skilled in the art from the following detailed description of the invention and the appended claims and the drawings in which Figures 1-7 show regression analysis correlations between HLMI of the high molecular weight component

and blend properties, Figures 8 and 9 show typical molecular weight distributions of blends of this invention.

In accordance with this invention it has been found that a mixture of a low molecular weight ethylene polymer and a high molecular weight ethylene polymer exhibits both desirable processing properties and excellent film properties when extruded into a polyolefin film. The polymer blends so composed are useful for the production of polyolefin film, particularly by blown tubing techniques, and for blow-molding (e.g. to produce bottles), pipe production and wire coating.

The low molecular weight ethylene polymer, the high molecular weight ethylene polymer and the blend are further characterized in Table I. The typical bimodal molecular weight distribution of the resin blends of this invention is shown for two different samples in Figure 8 and 9, respectively.

TABLE I

PROPERTIES OF THE ETHYLENE POLYMERS AND BLENDS

	High Molecular Weight Ethylene Polymer	Low Molecular Weight Ethylene Polymer	Blend
HLMI (g/10 min)			
generally	0.1-1.5	---	3-34
preferred	0.2-0.6	---	5-12
MI (g/10 min)			
generally	---	45-300	0.01-0.6
preferred	---	100-300	0.03-0.5
Density (g/cc)			
generally	about 0.930-0.955	about 0.945-0.975	.940-.965
preferred	about .930-.945	about .950-.975	.950-.960
Structure (Monomers)			
generally	Ethylene or Ethylene and 0 to 30 wt. % C_{3-10} olefins	Ethylene or Ethylene and 0 to 30 wt. % C_{3-10} olefins	---
preferred	Ethylene and 1 to 15 wt. % C_{3-7} olefins	0.5 to 5 wt. % C_{3-10} olefins	---
most preferred	Ethylene and 5 to 10 wt.% C_{4-10} olefins (random copolymer)	Ethylene ("Homopolymer" i.e. one that contains less than about 2 weight % C_{4-10} olefin comonomer, most preferably a true ethylene homopolymer)	---
Branching	essentially no branching other than short chain branching from comonomer	essentially linear	
Molecular Weight Distribution (SEC) (HI = M_w/M_n)			
generally	<10	<6	>18
preferred	4-9	2-4	20-35

The various polymer properties in this table and following tables are determined as follows:

MI (melt index, g/10 min, 190°C):	ASTM D 1238-65T, load of 2.16 kg
HLMI (High load melt index, g/10 min, 190°C):	ASTM D 1238-65T, load of 21.6 kg
Density(g/cc):	ASTM D 1505-68

M_w = weight average molecular weight, determined by size exclusion chromatography (SEC)

M_n = number average molecular weight, determined by size exclusion chromatography (SEC)

HI = heterogeneity index = M_w/M_n

The preferred polymers and blends have molecular weights and molecular weight distributions roughly as shown in the following table:

TABLE II

Component #1 (High Molecular Weight) Approximate Values	Typical Range
$M_w \sim 500,000$	400,000 to 700,000
$M_n \sim 70,000$	
$M_w/M_n \sim 7.5$	4 to 9
Component #2 (Low Molecular Weight)	
$M_w \sim 15,000$	10,000 to 20,000
$M_n \sim 5,000$	
$M_w/M_n \sim 3$	2 to 4
Blend	
$M_w \sim 270,000$	200,000 to 400,000
$M_n \sim 10,000$	
$M_w/M_n \sim 27$	20 to 35

The presently preferred ethylene polymers and copolymers within the limits set forth above are those produced with high productivity catalysts such as titanium/magnesium catalysts used in conjunction with organoaluminum cocatalysts. Such catalysts as well as polymerization processes to make such ethylene polymers are described in more detail in

European Patent Application No. 81 106 259.5 and 81 102 181.5 disclosure of which is herein incorporated by reference.

In accordance with the first embodiment of this invention a process to produce an ethylene polymer composition is provided. The process comprises blending the two ethylene polymers described above in relative quantities described below. The blending can be done by simply dry blending the two kinds of polymers in fluff (powder) form. Other possibilities to mix the polymers include melt blending in a pelletizing extruder. Banbury® mixers and single or twin screw extruders can be utilized. The preferred method is dry blending followed by melt blending. The blending conditions depend upon the blending technique employed. If a dry blending of the polymer fluff is the blending technique, the blending conditions may include temperatures from room temperature up to about 120° C and blending times in the range of a few seconds to minutes, e.g. 2 seconds to 5 minutes. If extrusion blending is used, the temperature of the polymers introduced into the extruder will be generally between room temperature and a temperature near the melting point of the polymer; the outlet temperature of the extrusion blended polymer will be in the range between the melting point of the polymer and up to 160° C above the melting point. The individual polymer particles usually remain in the extruder for a time of about 10 seconds to about 15 minutes. If solution blending techniques are employed the blending temperature will generally be 25 to 50° C above the cloud point of the solution involved.

Another embodiment of this invention is a polymer blend of the two ethylene polymers as defined above. Such a blend consists essentially of the two polymers and commonly used polymer additives such as antioxidants, UV stabilizers, fillers, pigments etc. The main polymer ingredients are present in this blend in quantities based on the total polymer as specified in Table III.

TABLE III

BLEND COMPOSITION (WEIGHT %)

	Generally	Preferred
High molecular weight ethylene polymer (HLMI 0.1 to 1.5)	40 to 70	about 50 to about 55
Low molecular weight ethylene polymer (MI 45-300)	60 to 30	about 50 to about 45

The resins blended are preferably selected from the HLMI and the MI ranges respectively so that a high molecular weight resin from the lower end of the range for HLMI values is blended with a low molecular weight resin from the higher end of the range for the MI values and vice versa.

Other embodiments of this invention are a method to produce an ethylene polymer film and the film so produced. The method of producing the ethylene polymer film includes extruding a molten web composed of the ethylene polymer blend defined above which is drawn down to the desired thickness, generally in the range of 0.1 to 5 mil. Extruding a flat film (width between 1 foot and 15 feet) and extruding a film tubing are both contemplated in this embodiment. The tubular extrusion with a blow/up ratio of tubing diameter to orifice die diameter in the range of about 2:1 to 10:1 is presently preferred. Typical dies have orifice diameters of 1" to 100".

The invention will be still more fully understood from the following examples which are intended to illustrate the invention and further preferred embodiments thereof without undue limitation of the scope of this invention.

The experimental methods and procedures employed in the following examples were as follows:

Ethylene Polymer Production

In a pilot plant several ethylene homopolymers and ethylene 1-hexene copolymers were produced with high activity titanium/magnesium catalysts. These catalysts are described in detail in the above cited European Patent Applications. Polymers produced were either high molecular weight or low molecular weight polymers as further specified in

the following examples. For stabilization during the processing the following additives were admixed with the polymers:

BHT (2,6-di-t-butyl-4-methylphenol)	0.05 weight %
DLTDP (dilauryl thiodipropionate)	0.03 weight %
Calcium stearate	0.04 weight %

In some of the examples 0.1 weight % of Irganox 1010® (tetrakis-[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane commercially available from Ciba-Geigy) was also added.

The mixing of the two ethylene polymer components was carried out in a variety of apparatus. A Henschel mixer was used to blend the fluff. A Farrel Banbury size 00, a Farrel 2FCM and a Davis-Standard 38 mm single screw extruder were used as shown in the following tables. The polymer blend obtained from the Banbury mixer was finished in a Foremost QG10-10 granulator, a Davis-Standard 150S 38 mm extruder or respectively a Cumberland 6 pelletizer.

The ethylene polymer blend was converted to a blown film using a 38 mm Davis-Standard extruder of 24-1 length/diameter ratio screw. The film die was 10.2 cm in diameter with a 0.56 mm die gap. An air ring was used to cool and support the ethylene polymer bubble in a film tower. The extrusion temperature was in the range of 250 ± 20° C. The film produced generally had a thickness of 1 mil. The blow/up ratio was 4:1 and the linear drawdown ratio was 5.5:1.

The various properties of the ethylene polymer film were measured as follows:

Dart Impact:

The dart impact resistance of the one mil film was measured using ASTM D 1709-75. This method measured the energy required to break the film upon impact of a free falling dart. This method established the weight of the dart dropped from a height of 26 inches which caused 50 percent of the samples to break. The staircase method was used to determine the 50 percent failure level, and the missile weight increment was 15 g.

Elmendorf Tear:

The Elmendorf tear resistance, called tear in Table XV, was measured using ASTM D 1922. This is a modification for polymer film

adapted from the Elmendorf tear test used for paper. This method determined the average force in grams per specimen required to propagate a tear through 2.5 inches of film. The method was used to rank relative tearing resistance of different blends.

Patterson Puncture:

The resistance to puncture/propagation of tear was measured by a modification of ASTM D 2582. This test method is used for determination of dynamic tear resistance or resistance to snagging of plastic film. The ASTM method was modified for lower weight carriages.

Spencer Impact:

Spencer impact was measured using ASTM D 3420. The following formula was used to obtain an impact value in joules.

$$E = RC/100$$

E = Energy to rupture, Joules
C = Apparatus capacity, 1.35 Joules
R = Scale Reading on a 0 to 100 scale.

This method was more rapid than dart impact and could be used as a control test while the film line was running. This test measured the energy necessary to burst and penetrate the center of a one mil thick specimen, mounted between two rings with a 3½ inch diameter.

Fish Eye:

Fish eye count or gel count was made on two sections of film one mil thick and one square foot in area. Only fish eyes greater than ten mils in at least one dimension were counted. In the case of film with fish eye count greater than 50 per square foot a five square inch section of film was counted.

Tensile Strength and Elongation:

Tensile strength and elongation were measured in accordance with ASTM D 638, 2"/min.

Shore Hardness:

Shore D hardness was measured in accordance with ASTM D 2240-68.

RDI:

Rheological distribution index (RDI) is an arbitrary rheological index value obtained from measurements made on a polymer sample with a Rheometrics Dynamic Spectrometer (Rheometric's Company). A

molten polymer sample is subjected to a sinusoidal, oscillating shear strain between two parallel circular plates at 190° C. The frequency of oscillation is varied from 10^{-1} to 5×10^{2} radians/sec. A log-log plot of frequency vs. dynamic loss modulus is made and the slope of the curve determined when the loss modulus is equal to 10^{5} dynes/cm^{2}. The reciprocal of the slope is defined as RDI. The larger the RDI value, the greater the shear response of the polymer. Since polymer shear response is related to its molecular weight distribution (the broader the distribution the greater the shear response) the RDI value is thought to provide a reliable indication of molecular weight distribution.

<u>Flexural Modulus, MPa</u>:

The flexural modulus is determined in accordance with ASTM D 790.

<u>ESCR (Bell)</u>:

The Environmental Stress Cracking Resistance was determined in accordance with ASTM D 1693-60 , condition A.

<u>Viscosity</u>:

The dynamic shear viscosity, in units of 10^{5} Poise, is obtained from the Rheometrics Dynamic Spectrometer as is the RDI. The viscosity reported is that at 0.1 radians/second (frequency of oscillation).

Throughout all of the following examples, the following abbreviations will be used.

PE: ethylene homopolymer

EHC: ethylene 1-hexene copolymer, 75-99 wt. % ethylene and 1 to 25 wt. % 1-hexene.

EXAMPLE I

In this example film was produced from commercially available ethylene polymer resins Hostalen® GM9255 (Hoechst), and TR130 polyethylene (Phillips Petroleum Company) produced with a chromium oxide catalyst, and an ethylene polymer blend as specified mixed in different equipment as shown in the following table. The film test results as well as the properties of the polymer blend used for the production of the film are given in the following Table IV.

In comparing polymers and blends, in a given series, constant conditions were employed and the film was extruded on the same day if at all possible.

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TABLE IV

FILM RESIN PROPERTIES

Ethylene Polymer :	Dart Impact g 26"/13"	Elmendorf Tear g MD/TD	Patterson Puncture Kg MD/TD	Spencer Impact J	Fish Eye Count count/ft^2 gel/char	Melt Index g/10 min.	HLMI g/10 min.	Density g/cc
Control:								
Hostalen GM9255	100/240	22/290	1.7/2.7	0.24	3/0.1	0.05	8.4	0.95[illegible]
TR130	<50/130	77/170	1.8/2.0	0.18	2.5/0.1	0.28	21.5	0.942
Blends:								
50 wt. % EHC 0.27 HLMI 0.936 g/cc 50 wt. % PE 280 MI 0.970 g/cc								
Banbury mixed	200/390	56/290	2.9/3.0	0.32	3.0/4.0	0.09	7.6	0.959
38 mm Davis-Standard Single Screw Extruder only	190/390	51/360	2.7/3.0	0.34	40/1.0	0.09	8.2	0.957
2FCM blended only	210/400	44/400	2.9/3.1	0.34	7.0/1.0	0.09	8.4	0.959

The data in Table IV compare the properties for the preferred ethylene polymer blend in accordance with this invention, which is an approximately 50/50 wt. % blend of the low molecular weight and the high molecular weight ethylene polymer with the film properties achieved with two commercial resins and three experimental blends. The ethylene polymer blend resulted in an improved impact, tear and puncture resistance compared to the commercial film resins even though measurable physical properties were similar. The fish eye count was increased when the mixing was scaled up to the 38 mm Davis-Standard single screw extruder but the char was reduced by the continuous mixing method. It is also to be noted that the blend obtained in the 2FCM apparatus had reduced fish eye count compared to the single screw extruder blend.

EXAMPLE II

In this example the influence of the MI (melt index) of the low molecular weight ethylene polymer component in the blend was tested. The components used and the results obtained as well as the mixing techniques employed are shown in the following Table V.

TABLE V

SLOT FILM STUDY OF EFFECT OF MELT INDEX OF LOW MOLECULAR WEIGHT COMPONENT

EHC 1.3 HLMI, 0.940 g/cc	55	55	55	55	55
PE 158 MI, 0.966 g/cc	45				
PE 67 MI, 0.968 g/cc		45			
PE 47 MI, 0.971 g/cc			45	45	45
Mixing:					
Henschel Powder Mix	yes	yes	yes	yes	yes
Force Feeder	yes	yes	yes	yes	yes
Screw Type	2.2/1SS(1)	2.2/1SS	2.2/1SS	2.2/1SS	DDD(2)
Static Mixer(3)	yes	yes	yes	yes	yes
Temp. °C	220	220	220	160	220
Results:					
Fish Eye Count/ft^2	564	840	192	312	132
Melt Index, g/10 min	0.23	0.22	0.23	0.23	0.19
HLMI, g/10 min	16.4	12.5	12.7	12.7	11.5
Density, g/cc	0.9577	0.9568	0.9559	0.9559	0.9550
RDI	1.58	1.52	1.44	1.49	1.53
ESCR, hours	>1000	>1000	>1000	>1000	>1000

(1)2.2/1SS is a single stage screw having a compression ratio of 2.2.
(2)DDD is a devolatilizing screw with a double Dulmage mixing section.
(3)Static mixer section (Kenics Co.) located between extruder and pelletizing die.

The results in Table V indicate that while the fish eye count was reduced by using a mixing screw, decreasing the melt temperature from 220°C to 160°C did not reduce the fish eye count. This is a significant and advantageous result because it shows that an increase in temperature does not increase the fish eye count. The data of this table also indicate that the melt index or molecular weight of the low molecular weight component was not a controlling factor in the fish eye count.

EXAMPLE III

The previous example was essentially repeated with a group of different resins. The ingredients and quantities used as well as the data obtained are shown in Table VI.

TABLE VI

EHC 0.22 HLMI, 0.936 g/cc	45	45	45	50	50	50	55	55	55
PE 158 MI, 0.966 g/cc	55			50			45		
PE 67 MI, 0.968 g/cc		55			50			45	
PE 47 MI, 0.971 g/cc			55			50			45
Mixing:									
Henschel Powder Mix	yes	yes	yes	yes	yes	yes	yes	yes	yes
Force Feeder	yes	yes	yes	yes	yes	yes	yes	yes	yes
Screw Type	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)
Static Mixer(3)	yes	yes	yes	yes	yes	yes	yes	yes	yes
Temp. °C	180	180	180	180	180	180	180	200	200
Results:									
Fish Eye Count/ft^2	1300	1600	2300	620	250	1000	280	60	230
Melt Index, g/10 min	0.10	0.08	0.09	0.06	0.06	0.06	0.05	0.04	0.05
HLMI, g/10 min	10.2	7.5	8.0	5.9	5.0	5.0	3.7	3.1	3.5
Density, g/cc	0.9611	0.9591	0.9581	0.9589	0.9591	0.9570	0.9581	0.9553	0.9562
RDI	1.75	1.76	1.73	1.57	1.68	1.67	1.54	1.55	1.[illegible]
ESCR, hours	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000	>1000

(2)(3)See footnotes of Table V.

The data in Table VI demonstrate a strong dependency of the fish eye count upon the quantity of high molecular weight polymer utilized. The higher the quantity of the high molecular weight component in the resin the lower the fish eye count became. Fish eye count and blend melt index are again shown to be independent of the melt index of the low molecular weight component.

EXAMPLE IV

The previous example was again essentially repeated with the components as shown in Table VII. In this experiment the high molecular weight polyethylene was not an ethylene 1-hexene copolymer but rather an ethylene homopolymer.

TABLE VII

Ethylene Polymers:									
PE 0.10 HLMI, 0.940 g/cc	45	45	45	50	50	50	55	55	55
PE 158 MI, 0.966 g/cc	55			50			45		
PE 67 MI, 0.968 g/cc		55			50			45	
PE 47 MI, 0.971 g/cc			55			50			45
Mixing:									
Henschel Powder Mix	yes	yes	yes	yes	yes	yes	yes	yes	yes
Force Feeder	yes	yes	yes	yes	yes	yes	yes	yes	yes
Screw Type	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)	DDD(2)
Static Mixer(3)	yes	yes	yes	yes	yes	yes	yes	yes	yes
Temp. °C	230	230	230	230	230	230	230	240	240
Results:									
Fish Eye Count/ft^2	2900	2000	3300	400	400	1400	100	190	250
Melt Index, g/10 min	0.02	0.02	0.03	0.013	0.01	0.014	0.006	0.007	0.007
HLMI, g/10 min	6.8	4.4	5.8	4.3	3.5	3.4	2.3	1.90	1.79
Density, g/cc	0.9641	0.9635	0.9615	0.9634	0.9612	0.9609	0.9607	0.9605	0.9597
RDI	1.92	1.91	1.97	1.96	1.92	1.93	1.84	1.82	1.86
ESCR, hours	155	381	109	305	275	240	373	640	5[illegible]

(2)(3) See footnotes of Table V.

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The data in Table VII show the same trend as observed in the earlier examples, namely that the fish eye count goes down with increasing quantity of high molecular weight ethylene polymer. Additionally, however, the above data show that the environmental stress crack resistance is substantially reduced when an ethylene homopolymer is used as compared to the previous examples where an ethylene 1-hexene copolymer was used as the high molecular weight component.

EXAMPLE V

In this example various blends of 60 weight percent of high molecular weight resin and 40 weight percent of low molecular weight resin were tested. The polymers used and the results obtained as well as the mixing procedure are shown in Table VIII.

TABLE VIII

Ethylene Polymer:				
PE 47 MI, 0.9706 g/cc	40	40		
EHC 49 MI, 0.9543 g/cc			40	
EHC 45 MI, 0.9489 g/cc				40
PE 1.5 HLMI, 0.9522 g/cc			60	60
EHC 1.3 HLMI, 0.9447 g/cc		60		
EHC 1.3 HLMI, 0.9404 g/cc	60			
Mixing:				
Henschel Mix	yes	yes	yes	yes
Banbury Mix	yes	yes	yes	yes
Pelletize	yes	yes	yes	yes
Properties:				
Melt Index, g/10 min.	0.20	0.19	0.23	0.25
HLMI, g/10 min.	10.2	9.6	10.9	12.2
Density, g/cc	0.9560	0.9577	0.9550	0.9553
Flexural Modulus, MPa	1370	1520	1400	1260
ESCR, hours	>1000	>1000	87	87
Film Test Results:				
Dart Impact, g, 26"/13"	<50/100	<50/100	(surged)	<50/70
Elmendorf Tear, g, MD/TD[1]	60/150	50/130	No good	50/110
Patterson Puncture, Kg, MD/TD	2.4/2.6	2.2/2.7	film	1.7/2.3
Fish Eye Count, Hard Gel/Char	3/8	5/10	2/16	3/22

[1] MD is machine direction; TD is transverse direction.

The data in Table VIII again show a strong dependency of the environmental stress crack resistance upon the structure of the high molecular weight ethylene polymer utilized. Whereas the blend having an ethylene 1-hexene copolymer as the high molecular weight component shows very good environmental stress crack resistance, the blend containing an ethylene homopolymer as the high molecular weight ethylene polymer component in the blend shows a substantially reduced environmental stress crack resistance even though the blend densities and melt flows are very close.

EXAMPLE VI

In this example a blend of a low molecular weight ethylene homopolymer and a high molecular weight ethylene 1-hexene copolymer as indicated and specified in the following table were used with varying mixing techniques. The results are shown in Table IX.

TABLE IX

Ethylene Polymer:				
PE 47 MI, 0.9706 g/cc	45	45	45	45
EHC 1.3 HLMI, 0.9404 g/cc	55	55	55	55
Zinc Stearate, Part by Weight	0.05	0	0	0
Ethylene-bis-stearamide, Part by Weight	0	0.05	0.05	0
Mixing:				
Henschel Mix	yes	yes	yes	yes
Banbury Mix	yes	no	yes	no
Pelletize	yes	yes	yes	no
Properties:				
Melt Index, g/10 min.	0.47	0.42	0.25	fluff
HLMI, g/10 min.	28.7	27.1	14.0	feed
Density, g/cc	0.958	0.958	0.956	no
Flexural Modulus, MPa	1490	1500	1450	pellets
ESCR, hours	>1000	>1000	>1000	
Film Test Results:				
Dart Impact, g, 26"/13"	60/130	70/170	80/190	90/200
Elmendorf Tear, g, MD/TD	40/90	40/120	60/150	30/150
Patterson Puncture, Kg, MD/TD	1.7/2.2	1.6/2.1	2.4/2.8	1.7/2.5
Fish Eye Count, Hard Gel/Char	5/7	750/0	11/11	6/0

The right column of Table IX is particularly interesting since this run demonstrates the possibility for direct feeding of the polymer fluff mixture to a film extruder while obtaining excellent film test results. Thus no extruder or Banbury premixing was required in this run. A force feeder was used during the film extrusion to eliminate surging. The environmental stress crack resistance values for the pellet blends used in this example also were very good.

EXAMPLE VII

In this example the effect of the high molecular weight copolymer on the Dart impact strength was tested. The ethylene polymer components used and the results obtained are shown in Table X.

TABLE X

Ethylene Polymer:						
PE 47 MI, 0.9706 g/cc	55			50		
EHC 49 MI, 0.9543 g/cc		55			50	
EHC 45 MI, 0.9489 g/cc			55			50
PE 1.5 HLMI, 0.9522 g/cc		45	45		50	50
EHC 1.3 HLMI, 0.9447 g/cc	45			50		
Mixing:						
Henschel Mix	yes	yes	yes	yes	yes	yes
Pelletize	yes	yes	yes	yes	yes	yes
Kinetic Mixer	yes	yes	yes	yes	yes	yes
Banbury Mix	no	no	no	no	no	no
Properties:						
Melt Index, g/10 min	0.45	0.53	0.54	0.32	0.34	0.38
HLMI, g/10 min	29.1	33.8	33.9	20.2	20.2	22.2
Density, g/cc	0.9596	0.9558	0.9526	0.9598	0.9552	0.9525
Flexural Modulus, MPa	1680	1390	1280	1520	1340	1270
ESCR, hours	382	24	15	462	30	30
Film Test Results:						
Dart Impact, g, 26"/13"	79/160	<50/120	<50/120	82/190	65/160	<50/130
Elmendorf Tear, g, MD/TD	30/110	30/120	30/100	40/110	30/190	40/210
Patterson Puncture, Kg, MD/TD	1.7/1.8	1.6/1.7	1.6/1.8	1.9/2.2	1.7/2.0	1.7/1.8
Fish Eye Count, Hard Gel/Char	950/0	780/0	660/0	7.5/0.8	7.6/0.2	15/0.2

The data in Table X demonstrate that the dart impact strength is improved if the high molecular weight portion is a copolymer rather than the low molecular weight portion of the ethylene polymer composition. A further surprising result is shown in the above table. Even though in the first and the fourth run the density of the resin mixture was higher than in the second and the fifth run, respectively, the dart impact strength was superior. This is very unusual and surprising because density has a primary influence on dart impact. Superior dart impact is generally associated with lower density. This blend composition thus shows a clear and unexpected advantage over conventional polyethylene film resins in that resin blends with higher density show better dart impact strength than those with comparatively lower density when the preferred copolymer distribution is used. Again a substantial dependency of the environmental stress crack resistance upon the structure of the high molecular weight ethylene polymer component is apparent from the above data. These data confirm the previous finding that the environmental stress crack resistance is best when the high molecular weight ethylene polymer component is an ethylene/1-hexene copolymer. The table above also shows the reduced Fish Eye Count for the 50/50 weight percent blend.

The above runs also demonstrate the feasibility of the elimination of a Banbury mixing step.

EXAMPLE VIII

This example was carried out to demonstrate that a blend of ethylene polymers with a density above 0.960 could have a high Dart impact strength when made into blown film. The components used and the results obtained are again shown in Table XI.

Table XI

Ethylene Polymer:				
PE 158 MI, 0.9664 g/cc	60	60	60	60
EHC 0.22 HLMI, 0.9359 g/cc	40	40		
PE 0.10 HLMI, 0.9401 g/cc			40	40
Mixing:				
Henschel Mix	yes	yes	yes	yes
Banbury Mix	no	yes	no	yes
Pelletized	yes	yes	yes	yes
Static Mixer	no	no	no	no
Properties:				
Melt Index, g/10 min.	0.17	0.17	0.08	0.08
HLMI, g/10 min.	17.6	15.6	12.6	8.5
Density, g/cc	0.9623	0.9626	0.9643	0.9639
Flexural Modulus, MPa	1680	1650	1800	1620
ESCR, hours	>1000	>1000	126	282
Film Test Results:				
Dart Impact, g, 26"/13"	<50/120	150/250	<50/<50	180/340
Elmendorf Tear, g, MD/TD	30/180	50/180	40/120	40/390
Patterson Puncture, Kg, MD/TD	1.7/2.0	2.1/2.7	1.6/1.7	2.4/2.8

In the blends shown in Table XI very low HLMI polymers, i.e. ethylene polymers with high molecular weight, were used and they required more intensive mixing such as Banbury mixing in order to obtain good film properties. The data show, however, that the film properties are very good despite the fact that the blend density is above 0.96. ESCR again points out the significance of even small amounts of short branching in high molecular weight component.

EXAMPLE IX

Ethylene polymer resin blends were fabricated from ethylene polymers and using mixing techniques as indicated in the following table. The properties of the polymer blend as well as the film test results are also shown in Table XII. In the series employing extruder mixing, each composition was prepared with the indicated screw type.

TABLE XII

Ethylene Polymer:					
PE 158 MI, 0.9664 g/cc	60	60	60	60	60
EHC 0.22 HLMI, 0.9359 g/cc	40	40	40	40	40
Mixing:					
Henschel Mix	yes	yes	yes	yes	yes
Banbury Mix	no	no	no	no	no
Davis-Standard					
2.2/1SS Screw(1)	yes	no	no	no	no
3.0/1SS Screw(2)	no	yes	no	no	no
TSD Screw(3)	no	no	yes	no	no
SSM Screw(4)	no	no	no	yes	no
DDD Screw(5)	no	no	no	no	yes
Static Mixer	yes	yes	yes	yes	yes
Properties:					
Melt Index g/10 min	0.14	0.16	0.15	0.15	0.10
HLMI, g/10 min	15.7	20.4	18.6	19.8	19.6
Density, g/cc	0.9633	0.9628	0.9627	0.9624	0.9622
Flexural Modulus, MPa	1670	1670	1640	1690	1670
ESCR, hours	>1000	>1000	>1000	>1000	>1000
Film Test Results:					
Dart Impact, g, 26"/13"	<50/<50	<50/<50	<50/<50	<50/<50	<50/<50
Elmendorf Tear, g, MD/TD	27/270	28/190	28/160	30/160	27/180
Patterson Puncture, Kg, MD/TD	1.6/1.9	1.6/1.8	1.5/1.7	1.6/1.7	1.6/1.6

(1) Same as footnote 1, Table V.

(2) 3.0/1SS is a single stage screw having a compression ratio of 3.0.

(3) TSD is a two-stage devolatilizing screw.

(4) SSM is a single screw with a Maddox mixing section.

(5) Same as footnote 2, Table V.

The poor results in Table XII, as indicated by dart impact data, for these blends which all contain less than 50% high molecular weight component, emphasizes the preference of a composition having at least 50% high molecular weight component. Banbury mixing is generally required for good results only if the composition falls below 50% in high molecular weight component.

EXAMPLE X

In this example resin blends were made using again ethylene polymers in quantities as specified in Table XIII. This table also shows the properties of the blend and the film test results.

TABLE XIII

Ethylene Polymer:						
Hostalen GM, 9255	100					
TR130		100				
PE 158 MI, 0.9664 g/cc			60(1)			
EHC 0.10 HLMI, 0.9401 g/cc			40			
PE 275 MI, 0.9696 g/cc				50	50	50
EHC 0.27 HLMI, 0.9355 g/cc				50	50	50
Irganox 1010 (Part by Weight)			0.1	0.1	0.1	0.1
Mixing:						
Commercial Resin Control	yes	yes	no	no	no	no
Henschel Mix	no	no	yes	yes	yes	yes
Double Pass-Double Letdown(2)	no	no	yes	no	no	no
DDD Screw	no	no	yes	no	no	no
Banbury Mix	no	no	no	yes	no	no
Pelletize, Davis-Standard:	no	no	yes	yes	yes	yes
2.2 1/SS Screw	no	no	no	yes	yes	yes
Static Mixer	no	no	yes	yes	yes	yes
Properties:						
Melt Index, g/10 min	0.05	0.28	0.07	0.09	0.09	0.09
HLMI, g/10 min	8.4	21.5	14.9	7.6	8.2	7.2
Density, g/cc	0.9573	0.9417	0.9653	0.9592	0.9566	0.9575
Flexural Modulus, MPa	1570	918	1820	1540	1580	1490
ESCR, hours	>1000	>1000	132	>1000	>1000	>1000
RDI	2.14	1.72	1.81	1.48	1.55	1.59
Film Test Results:						
Dart Impact, g, 26"/13"	100/240	<50/130	<50/<50	200/390	190/390	180/370
Elmendorf Tear, g, MD/TD	20/290	77/170	26/150	56/290	51/360	45/290
Patterson Puncture, Kg, MD/TD	1.7/2.7	1.8/1.95	1.5/1.6	2.9/3.0	2.7/3.0	2.7/2.9
Spencer Impact, Joules	0.24	0.18	0.09	0.32	0.34	0.34
Fish Eye Count, Gel/Char	3/0.1	2.5/0.1	40/1.0	3.0/4.0	40/1.0	68/0

(1) This recipe gave poor film properties with 2-FCM mix only.

(2) The low molecular weight resin was blended with about 50 volume % of the high molecular weight resin, then extruded and pelletized. The pellets were blended with the remainder of the high molecular weight resin, then extruded and pelletized again.

The results of this table in this example again seem to indicate that for obtaining a satisfactory blend when using 60 parts by weight of the low molecular weight ethylene polymer and 40 parts by weight of a high molecular weight resin, a Banbury premixing or another intensive premixing is required for the use of the resin in film making processes.

The last three runs show that the ethylene polymer mixture of this invention results in superior resins for film production. The performance exceeds that expected for polyethylene of this density and melt flow. The last two runs of this example are duplicate runs to test the reproducibility of the results which is, as can be seen, excellent.

EXAMPLE XI

A. Polymers

The polymers used in this example were all prepared in a pilot plant loop reactor using the Ti/Mg catalyst as described in European Patent Application 81 106 259.5. Relatively narrow molecular weight distribution polymers of widely different molecular weights were produced with this catalyst by changing the hydrogen concentration in the reactor. These polymers are recovered as fine powders or fluff which are easily blended by various techniques such as a Henschel mixer. A description of the different base resins used in this program is presented in Table XIV. All copolymers used 1-hexene as the comonomer.

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TABLE XIV

DESCRIPTION OF BLEND COMPONENTS

A. High Molecular Weight Polymers (HMWP)

HMWP	Density (g/cc)	HLMI (g/10 min.)
1H	0.9360	0.24
2H	0.9355	0.30
3H	0.9380	0.37
4H*	0.9490	1.41
5H*	0.9500	1.56
6H*	0.9480	0.89
7H	0.9445	1.40
8H	0.9419	2.04
9H	0.9388	1.80
10H	0.9393	1.48
11H	0.9377	1.71
12H	0.9331	1.41
13H	0.9312	1.45

B. Low Molecular Weight Polymers (LMWP)

LMWP	Density (g/cc)	Melt Index (g/10 min.)
20L*	0.9675	67
21L*	0.9696	275
22L*	0.9700	146
23L*	0.9700	212
24L*	0.9690	108
25L	0.9700	150
26L	0.9600	98
27L	0.9550	106

*indicates homopolymers. All others are 1-hexene copolymers.

B. Mixing and Compounding

For stabilization during processing 0.05 weight % BHT, 0.03 weight % DLTDP and 0.04 weight % calcium stearate were added to the fluff in the Henschel mixer.

Mixing and pelletizing involved the following steps: 1. Blends of high and low molecular weight fluff were weighed to give the desired ratio. 2. The powder blends were mixed for three minutes at high speed in the Henschel mixer with stabilizers. 3. The powder blends were force fed to the 1.5 inch Davis-Standard extruder with nitrogen protection. The temperature zones on the extruder were set at 221 C. Screw speed was 90 rpm. Extrusion rate was in the range of 30 to 40 pounds per hour. The screw had a 3:1 compression ratio and a 24:1 length to diameter ratio. A 40/80/40 mesh screen pack was used. The six hole

die had 1/8 inch holes. A Cumberland Six Chopper was used for pelletizing. Melt temperatures were in the 230 to 250° C range.

C. Film Blowing

The blends were converted to blown film using a 1.5 inch Davis-Standard extruder with a four inch Sano die with a Sano tower and take-off equipment. The Sano die was a bottom fed spiral design with a 0.76 mm die gap. The die was designed for use with high density, high molecular weight polyethylene. The extruder was a 1.5 inch Davis-Standard with a 24:1 length to diameter ratio. The feed screw had a 2.2:1 compression ratio. A 20/20 mesh screen pack was used. Only one mil film was used for evaluation. The blow-up ratio was 4:1. The frost line height was 26 inches, and the melt temperature was in the range of 230 to 265 C. Take-off speed was 31 feet/minute.

D. Film Evaluation

The film was evaluated by measuring a variety of properties. The test methods used are as described above.

The results obtained with the various blends are shown in the following tables.

TABLE XV

SUMMARY OF BLEND PROPERTIES

BLEND NO.	1	2	3	4	5	6	7
High MW Component:				13H			
HLMI, g/10 min.				1.45			
Density, g/cc				0.9312			
Concentration, wt. %	50	52	54	56	58	60	62
Low MW Component:				26L			
MI				98			
Density				0.9600			
Concentration, wt. %	50	48	46	44	42	40	38
Blend Properties							
MI, g/10 min.	0.36	0.32	0.28	0.23	0.20	0.22	0.11
HLMI, g/10 min.	23.7	20.7	16.8	13.6	12.2	12.0	8.2
Density, g/cc	0.9475	0.9473	0.9466	0.9455	0.9444	0.9446	0.9438
Flexural Modulus, MPa	1057	1063	1089	1023	1004	1017	879
Tensile Yield, MPa	25.2	24.5	24.2	23.9	23.8	23.6	23.5
Tensile Break, MPa	34.5	34.7	37.6	37.5	38.8	37.7	37.8
Elongation, %	1070	1060	1320	1440	1700	1310	1630
Hardness, Shore D	65	65	65	65	65	64	64
Bell ESCR, hrs	>1000	>1000	>1000	>1000	>1000	>1000	>1000
Viscosity, Poise $X10^{-5}$	2.5	2.8	3.1	3.6	4.1	3.3	6.4
RDI	1.56	1.54	1.51	1.48	1.54	1.53	1.58
Film Properties							
Dart Impact, g, 26"	110	140	140	140	150	150	120
Spencer Impact, J	0.26	0.31	0.28	0.30	0.34	0.34	0.28
MD Tear, g	48	53	68	60	65	64	66
TD Tear, g	160	205	210	245	250	280	225
Fish Eyes, ft^{-2}	39	22	16	14	12	5	5

(1) See Table XIV for characterization of blend components.

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	8	8A	8B
High MW Component:		3H	
HLMI, g/10 min.		0.37	
Density, g/cc		0.9380	
Concentration, wt. %		50	
Low MW Component:		23L	
MI, g/10 min.		212	
Density, g/cc		0.9700	
Concentration, wt. %		50	
Blend Properties			
MI, g/10 min.	0.10	0.09	0.11
HLMI, g/10 min.	9.4	9.1	10.0
Density, g/cc	0.9578	0.9579	0.9582
Flexural Modulus, MPa	1543	1550	1567
Tensile Yield, MPa	-	-	-
Tensile Break, MPa	-	-	-
Elongation, %	-	-	-
Hardness, Shore D	-	-	-
Bell ESCR, hrs	-	-	-
Viscosity, Poise $X10^{-5}$	-	-	-
RDI	-	-	-
Film Properties			
Dart Impact, g, 26"	210	190	190
Spencer Impact, J	0.41	0.41	0.42
MD Tear, g	34	39	30
TD Tear, g	300	320	410
Fish Eyes, ft^{-2}	30	50	400

Notes: Three separate blends were identically prepared and converted into film. The blend and film properties are similar except for blend 8B which displays very high TD tear and abnormally high fish eyes. The reason for the high fish eye count is not known.

Dashes indicate no properties were determined.

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	9	10	9A	10A	11
High MW Component:			1H		
HLMI, g/10 min.			0.24		
Density, g/cc			0.9360		
Concentration, wt. %			50		
Low MW Component:	27L	26L	27L	26L	24L
MI, g/10 min.	106	98	106	98	108
Density, g/cc	0.9550	0.9600	0.9550	0.9600	0.9690
Concentration, wt. %	50	50	50	50	50
Blend Properties					
MI, g/10 min.	0.07	0.07	0.06	0.06	0.06
HLMI, g/10 min.	6.7	7.0	5.1	5.4	5.0
Density, g/cc	0.9490	0.9512	0.9492	0.9524	0.9578
Flexural Modulus, MPa	1103	1250	1108	1250	1400
Tensile Yield, MPa	24.8	25.6	24.5	25.9	27.8
Tensile Break, MPa	38.0	37.6	37.0	39.1	31.0
Elongation, %	1420	1140	1480	1300	820
Hardness, Shore D	64	63	63	65	66
Bell ESCR, hrs	>1000	>1000	>1000	>1000	>1000
Viscosity, Poise $X10^{-5}$	10.0	9.8	9.7	10.0	9.6
RDI	1.75	1.72	1.75	1.71	1.71
Film Properties					
Dart Impact, g, 26"	230	230	210	200	240
Spencer Impact, J	0.49	0.61	0.50	0.57	0.57
MD Tear, g	67	67	53	46	49
TD Tear, g	290	330	290	340	220
Fish Eyes, ft^{-2}	660	1000	750	1200	1100

Note: Blends 9, 9A and 10, 10A are duplicates.

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	12	12A	12B	12C
High MW Component:			5H	
HLMI, g/10 min.			1.56	
Density, g/cc			0.9500	
Concentration, wt. %			62	
Low MW Component:			24L	
MI, g/10 min.			108	
Density, g/cc			0.9690	
Concentration, wt. %			38	
Blend Properties				
MI, g/10 min.	0.14	0.13	0.13	0.12
HLMI, g/10 min.	10.0	9.4	9.6	8.8
Density, g/cc	0.9580	0.9600	0.9600	0.9598
Flexural Modulus, MPa	1667	1613	1610	1594
Tensile Yield, MPa	29.2	29.0	28.8	29.0
Tensile Break, MPa	40.1	38.5	39.6	43.0
Elongation, %	1200	1100	1200	1400
Hardness, Shore D	68	68	68	67
Bell ESCR, hrs	147	147	154	101
Viscosity, Poise $X10^{-5}$	-	-	-	-
RDI	1.56	1.56	1.57	1.59
Film Properties				
Dart Impact, g, 26"	110	110	96	84
Spencer Impact, J	0.30	0.24	0.28	0.30
MD Tear, g	30	25	28	30
TD Tear, g	170	130	110	110
Fish Eyes, ft^{-2}	3.5	1.0	0.5	1.5

Notes: Four separate blends of identical composition were prepared and converted into film.

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	13	14
High MW Component:	4H	6H
HLMI, g/10 min.	1.41	0.89
Density, g/cc	0.9490	0.9480
Concentration, wt. %	62	56
Low MW Component:	24L	25L
MI, g/10 min.	108	150
Density, g/cc	0.9690	0.9700
Concentration, wt. %	38	44
Blend Properties		
MI, g/10 min.	0.20	0.10
HLMI, g/10 min.	8.9	7.7
Density, g/cc	0.9597	0.9609
Flexural Modulus, MPa	1570	1570
Tensile Yield, MPa	29.3	28.0
Tensile Break, MPa	39.3	33.2
Elongation, %	1200	980
Hardness, Shore D	65	67
Bell ESCR, hrs	147	173
Viscosity, Poise $X10^{-5}$	3.4	6.0
RDI	1.44	1.63
Film Properties		
Dart Impact, g, 26"	45	130
Spencer Impact, J	0.28	0.28
MD Tear, g	34	33
TD Tear, g	250	130
Fish Eyes, ft^{-2}	10	10

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TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	15	16	17	18	19	20
High MW Component:		7H			8H	
HLMI, g/10 min.		1.40			2.04	
Density, g/cc		0.9445			0.9419	
Concentration, wt. %	59	59	55	62	63	62.5
Low MW Component:	27L	22L	20L	27L	22L	20L
MI, g/10 min.	106	146	67	106	146	67
Density, g/cc	0.9550	0.9700	0.9680	0.9550	0.9700	0.9680
Concentration, wt. %	41	41	45	38	37	37.5
Blend Properties						
MI, g/10 min.	0.17	0.18	0.12	0.21	0.21	0.15
HLMI, g/10 min.	10.7	10.6	9.5	10.6	10.6	8.4
Density, g/cc	0.9510	0.9570	0.9547	0.9487	0.9547	0.9527
Flexural Modulus, MPa	1274	1566	1551	1189	1353	1374
Tensile Yield, MPa	26.8	29.8	30.1	25.7	28.4	28.1
Tensile Break, MPa	38.1	35.7	33.4	36.9	38.1	39.4
Elongation, %	1300	1000	900	1200	1100	1100
Hardness, Shore D	65	67	67	65	67	67
Bell ESCR, hrs	424	>1000	>1000	>1000	>1000	>1000
Viscosity, Poise X10^{-5}	3.9	4.1	4.9	3.6	3.7	4.5
RDI	1.51	1.48	1.53	1.45	1.43	1.49
Film Properties						
Dart Impact, g, 26"	100	85	110	76	79	86
Spencer Impact, J	0.31	0.30	0.28	0.26	0.30	0.28
MD Tear, g	47	37	30	41	36	31
TD Tear, g	200	210	200	230	210	200
Fish Eyes, ft^{-2}	9	9	9	3	3	3

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	21	22	23	24	25	26
High MW Component:		9H			10H	
HLMI, g/10 min.		1.80			1.48	
Density, g/cc		0.9388			0.9393	
Concentration, wt. %	58	61	63	60	59	59
Low MW Component:	27L	22L	20L	27L	22L	20L
MI, g/10 min.	106	146	67	106	146	67
Density, g/cc	0.9550	0.9700	0.9680	0.9550	0.9700	0.9680
Concentration, wt. %	42	39	37	40	41	41
Blend Properties						
MI, g/10 min.	0.26	0.25	0.17	0.20	0.20	0.20
HLMI, g/10 min.	14.0	14.0	8.7	11.0	11.0	10.0
Density, g/cc	0.9482	0.9540	0.9528	0.9476	0.9546	0.9536
Flexural Modulus, MPa	1165	1432	1368	1138	1437	1400
Tensile Yield, MPa	24.4	27.8	27.3	24.3	27.6	28.1
Tensile Break, MPa	37.3	38.9	40.9	37.7	38.6	43.1
Elongation, %	1600	1100	1100	1500	1200	1500
Hardness, Shore D	65	66	66	65	66	67
Bell ESCR, hrs	>1000	>1000	>1000	>1000	>1000	>1000
Viscosity, Poise $X10^{-5}$	3.2	3.2	4.2	4.0	4.2	4.1
RDI	1.48	1.45	1.45	1.46	1.48	1.45
Film Properties						
Dart Impact, g, 26"	73	110	130	92	100	120
Spencer Impact, J	0.23	0.35	0.32	0.27	0.28	0.31
MD Tear, g	39	44	51	49	36	43
TD Tear, g	210	270	310	260	300	250
Fish Eyes, ft^{-2}	20	28	12	5	25	6

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	27	28	29
High MW Component:		11H	
HLMI, g/10 min.		0.71	
Density, g/cc		0.9377	
Concentration, wt. %	60.7	61	60.6
Low MW Component:	27L	22L	20L
MI, g/10 min.	106	146	67
Density, g/cc	0.9550	0.9700	0.9680
Concentration, %	39.3	39	39.4
Blend Properties			
MI, g/10 min.	0.28	0.30	0.25
HLMI, g/10 min.	13.0	15.0	12.0
Density, g/cc	0.9471	0.9534	0.9524
Flexural Modulus, MPa	1102	1373	1376
Tensile Yield, MPa	24.7	27.4	27.2
Tensile Break, MPa	37.7	38.1	39.9
Elongation, %	1600	1100	1100
Hardness, Shore D	65	66	66
Bell ESCR, hrs	>1000	>1000	>1000
Viscosity, Poise $X10^{-5}$	3.0	2.9	3.3
RDI	1.42	1.43	1.41
Film Properties			
Dart Impact, g, 26"	83	89	86
Spencer Impact, J	0.27	0.27	0.28
MD Tear, g	45	40	46
TD Tear, g	210	180	180
Fish Eyes, ft^{-2}	5	6	29

TABLE XV (continued)

SUMMARY OF BLEND PROPERTIES

BLEND NO.	30	31	32	33	34	35
High MW Component:		12H			13H	
HLMI, g/10 min.		1.41			1.45	
Density, g/cc		0.9331			0.9312	
Concentration, wt. %	59.1	58.8	56.4	59.3	59	56.9
Low MW Component:	27L	22L	20L	27L	22L	20L
MI, g/10 min.	106	146	67	106	146	67
Density, g/cc	0.9550	0.9700	0.9675	0.9550	0.9700	0.9675
Concentration, wt. %	40.9	41.2	43.6	40.7	41	43.1
Blend Properties						
MI, g/10 min.	0.22	0.21	0.21	0.22	0.22	0.23
HLMI, g/10 min.	13.0	12.0	13.0	13.0	13.0	12.0
Density, g/cc	0.9490	0.9499	0.9500	0.9433	0.9489	0.9494
Flexural Modulus, MPa	1018	1268	1255	972	1236	1226
Tensile Yield, MPa	22.5	25.1	26.9	23.0	26.1	26.5
Tensile Break, MPa	37.0	38.7	38.3	36.4	38.4	39.7
Elongation, %	1800	1200	1100	1700	1400	1300
Hardness, Shore D	64	66	65	63	66	65
Bell ESCR, hrs	>1000	>1000	>1000	>1000	>1000	>1000
Viscosity, Poise $X10^{-5}$	3.0	3.8	3.8	3.5	3.2	3.7
RDI	1.52	1.46	1.51	1.50	1.52	1.47
Film Properties						
Dart Impact, g, 26"	140	150	120	130	150	150
Spencer Impact, J	0.32	0.32	0.31	0.30	0.34	0.32
MD Tear, g	57	52	48	64	57	53
TD Tear, g	330	300	250	260	280	230
Fish Eyes, ft^{-2}	30	7	13	11	32	24

Some commercially available film resins were converted into film as described. The properties found are shown in Table XVI together with the properties of some of the films/resins blends of this invention.

DISCUSSION OF RESULTS

A. Effects of Ratio of Components

One of the most important facts discovered in this work relating to film resins was that, in order to get uniform, homogeneous blends from two widely different molecular weight polymers using continuous processing equipment, it is preferred that >50% by weight of the blend be of the high molecular weight component. This is not necessarily true if batch processing equipment, such as a Banbury, is used to homogenize the mixture.

The explanation for this phenomenon may be that at compositions of less than 50% high molecular weight polymer, the low molecular weight polymer becomes the continuous phase. Due to the extremely low viscosity of the low molecular weight polymer, it is very difficult to apply the necessary shear stresses to the high molecular weight particles to make them disperse uniformly. However, when the concentration of high molecular weight polymer exceeds 50%, it becomes the continuous phase and can easily transmit the shear stresses to the low molecular weight particles. In order to be safe and achieve the best dispersion, it is preferred that the film composition contains at least 52% high molecular weight polymer.

The effects of film blend composition is presented in Table XV, blends 1 through 7. The film fish eye count is a convenient method of measuring the homogeneity of the blend. Note that the fish eye count was at a high level of $39/ft^2$ for the 50/50 blend, but decreased to $5/ft^2$ for the 60/40 blend. Also, the film tear strength improves with increasing high molecular weight polymer content. The exact degree of dispersion for any particlar blend will depend upon the capabilities of the equipment used. However, the relative effect of concentration would be expected to apply in any equipment.

TABLE XVI

COMPARISON OF COMMERCIAL FILM RESINS WITH INVENTION BLENDS

	Commercial Film Resins		Examples of Invention Blends			
	Hizex 7000F	Hostalen GM9255F	Blend No. 8A	Blend No. 11	Blend No. 10A	Blend No. 10
Melt Index, g/10 min.	0.03	0.06	0.09	0.06	0.06	0.07
HLMI, g/ 10 min.	10.1	9.7	9.1	5.0	5.4	7.0
Density, g/cc	0.9533	0.9578	0.9579	0.9578	0.9524	0.9512
Flexural Modulus, MPa	1327	1476	1550	1400	1250	1250
Tensile @ yield, MPa	28.6	27.0	N.A.	27.8	25.9	25.6
Tensile @ Break, MPa	16.7	39.2	N.A.	31.0	39.1	37.6
Elongation, %	90	1143	N.A.	820	1300	1140
Hardness, Shore D	68	66	N.A.	66	65	63
Bell ESCR, hrs	>1000	>1000	N.A.	>1000	>1000	>1000
Dart Impact, g, (26")	195	179	190	240	200	230
Spencer Impact, J	0.356	0.359	0.41	0.57	0.57	0.61
Elmendorf Tear, g						
MD	53	38	39	49	46	67
TD	128	100	320	220	340	330
Fish Eyes, ft^{-2}	4	10	50	1100	1200	1000

The results obtained for blends 8-11 indicate that blends exhibiting excellent impact properties, high tear strengths, high ESCR values and acceptable to high flexural modulus values are obtained with a 50/50 weight percent blend of high molecular weight and low molecular weight components. The high molecular weight component had a HLMI of about 0.2-0.4 with a density of about 0.935 g/cc while low molecular weight polymers having MI values ranging from about 100-210 and densities ranging from about 0.955-0.970 g/cc were employed. The data show that the high fisheye counts (660 to 1200) for blends 9-11 can be substantially reduced by approximately doubling the MI of the low molecular weight component, e.g. from about 100 to about 200.

In the series of blends 12-35 the high molecular weight component varied from 55-63 weight percent, the HLMI varied from about 0.9-2 and the density ranged from about 0.931-0.950 g/cc. The low molecular component varied from 45-37 weight percent, the MI varied from about 70-145 and the density ranged from about 0.955-0.970 g/cc. All of the blends exhibited a low fisheye count (0.5-29) showing the importance of having greater than 50 weight percent high molecular weight component to accomplish a homogeneous blend.

As the density of the high molecular weight component decreased from about 0.950 g/cc of blend 12 to about 0.931 g/cc of blend 35 the results show that a substantial increase in Dart impact, Elmendorf tear and ESCR values were obtained. That is, Dart impact increased from 45 to 150 g, the MD tear increased from 25 to 64 g, the TD tear increased from 110 to 330 g and ESCR increased from 101 to greater than 1000 hours. The MI, density and flexural modulus of the resulting blends depended upon the values of the high and low molecular weight components.

The data in Table XVI demonstrate at approximately equal blend MI and density values relative to Hizex and Hostalen commercial resins that the invention blends generally exhibit superior Elmendorf tear, Dart impact and Spencer impact values. However, the invention blends have unacceptably high fisheyes for film applications but may be suitable for other applications such as blow molded or injection molded containers and the like.

Based on the data presented, an invention blend, when optimized for film applications, is calculated to have acceptably low fisheyes and the physical properties given in Table XVII.

The calculated data given in Table XVII suggest that an optimized blend compared to commercial resins of similar melt index and density values will exhibit a superior balance of impact strength and tear strength.

The molecular weight distribution obtained with invention blends by gel permeation chromatography is demonstrated in Figures 8 and 9. They are clearly bimodal in character. Figure 9 is based on a previously unreported 50/50 blend of high molecular weight polymer 2H and low molecular weight polymer 21L.

Multiple regression analyses on the data obtained have been made; they show that the weight fraction of high molecular weight polymer has a negative effect upon the HLMI, MI and density of the blend. Increasing this variable has a positive effect upon both the MD and TD tear strength. Surprisingly, the dart and Spencer impact strengths were not significantly affected by the concentration of high molecular weight component over the range of compositions studied. The blends were composed of between 50 and 60% high molecular-weight polymer. This relatively narrow range was desirable for two reasons. (1.) As discussed above, there is a practical or economical lower limit for the film resin blend of 50% high molecular weight component due to the homogenization problem. (2.) The melt index and high load melt index drop rapidly as the fraction of high molecular weight polymer increases. Thus, processability deteriorates at higher levels. This rather restricted range accounts for the fact that this variable does not show up as a statistically significant factor in the regression analysis of the dart and Spencer impact strength.

B. Effects of Molecular Weights of Components

The molecular weight (here described by HLMI and MI) of the high molecular weight component is the second most important factor in determining the properties of a film resin blend. Figures 1-7 illustrate the effects of this variable. Note, for example, that a HLMI of the high MW component below about 0.6 results in dart impact strength above 200 grams (Figure 4). Also, the tear strength and Spencer impact strength are all functions of this variable. Thus, there is a definite advantage in connection with film resin applications in keeping the HLMI of the high molecular weight component as low as possible. Low HLMI values of the high molecular weight component make it difficult to maintain the

melt index and HLMI of the blend at a sufficiently high level to achieve good processability while still adhering to the >50% rule discussed above.

The molecular weight of the low molecular weight component also enters into consideration but only to a minor extent. The melt index of the low molecular weight component does not appear as a significant variable in any of the film property regression analyses (see Table III). In fact, it is only important in determining the HLMI (but not the MI) of the blend. It appears that this component acts only as a lubricant or diluent to affect the HLMI of the blend. Thus, it is important to keep the MI of the low molecular weight material as high as possible in order to keep the HLMI of the blend sufficiently high to achieve good processability. Most preferably, the MI of the low molecular weight component is at least 200. The calculations used to prepare Figures 1-7 are all based on a blend melt index of 250 for the low molecular weight component.

C. Effects of Densities of Components

The third most important variable in determining the film properties of a blend is the density of the high molecular weight component. This varaible has a negative coefficient in each of the film property regression equations except the Spencer impact equation, where it was not significant. Thus, there is a definite advantage in keeping the density of the high molecular weight component as low as possible for maximum film properties. Of course, this must also be balanced against any specifications on density and stiffness.

On the other hand, the density of the low molecular weight component only shows up as significant in the regression equations for blend density and MD tear strength. Even in these cases it only has about 1/3 the effect of the density of the high molecular weight component. Thus, in order to achieve a high blend density and stiffness with high film strength properties it is best to use a high density low molecular weight component and a low density high molecular weight component. In other words, there is a definite advantage to placing the comonomer in the high molecular weight end of the molecular weight distribution of the blend. This is one of the advantages of using a blend approach to optimizing a polymer's molecular structure. There is

no known way of controlling the distribution of comonomer with a single reactor product.

D. Comparison With Competitive Resins

Data for two leading commercial high molecular weight film resins, Hizex 7000F and Hostalen GM 9255F, are presented in Table XVI and compared with several of the inventions blend polymers. These films were all produced under identical conditions. Inspection of these results shows that the invention blends are generally superior to the commercial resins in all film properties. The greatest advantage for the blends appears in the very important TD tear strength where the blends of this invention surpass the commercial resins by a factor of at least 2.

The mathematical models of the blend resin properties of this invention may also be used to formulate a resin to match the HLMI, MI and density of a commercial polymer. Table XVII illustrates these results for a blend which exactly matches the melt index, HLMI and density of Hostalen GM 9255F.

TABLE XVII

COMPARISON OF COMMERCIAL FILM RESINS WITH CALCULATED PROPERTIES OF OPTIMIZED INVENTION BLEND

	Competitive Resins		Calculated Blend*		
	Hizex 7000F	Hostalen GM9255F	Calculated Values	95% Confidence Limits	
Melt Index	0.03	0.06	0.06	0.02	0.10
HLMI	10.1	9.7	9.7	5.5	13.9
Density, g/cc	0.9533	0.9578	0.9577	0.9555	0.9600
Dart Impact, g	195	179	200	190	210
Spencer Impact, J	0.356	0.359	0.46	0.43	0.49
Elmendorf Tear, g					
MD	53	38	41	35	47
TD	128	100	280	220	350

*Blend Composition

High MW Component: HLMI = 0.35 g/10 min.
Density = 0.940 g/cc
Weight Fraction = 52%

Low MW Component: Melt Index = 300 g/10 min.
Density = 0.970 g/cc
Weight Fraction = 48%

E. Comparison of Hostalen Film Resin With Invention Film Resin Blend

A commercially available film resin was compared with the blend of this invention with the following results:

TABLE XVIIA

	Invention Blend*	Hostalen GM 9255F
HLMI, g/10 min.	7.4	9.7
MI, g/10 min.	0.09	0.06
Density, g/cc	0.946	0.9578
Dart Impact, g, 26"	213	190
Spencer Impact, J	0.55	0.41
Elmendorf Tear, g		
MD	37	38
TD	394	100
Fisheyes, ft^{-2}	12	10
Film Thickness, mils	1.0	1.0
Blow Up Ratio	4:1	4:1

*Blend Composition

High MW Component: HLMI = 0.36 g/10 min.
Density = 0.9340 g/cc
Weight Fraction = 52%

Low MW Component: MI = 112 g/10 min.
Density = 0.9571 g/cc
Weight Fraction = 48%

The results in Table XVIIA show the invention blend to be superior to the commercial resin in dart and Spencer impact values, equivalent in MD Elmendorf tear and about 4-fold better in TD Elmendorf tear. The fisheye content of each film is about the same. Note that film properties of this polymer are all significantly superior to those of the Hostalen resin. Thus, both the actual, observed blend data and the predictions from the models are in agreement with the conclusion that a superior film resin can be produced by this technique.

F. Environmental Stress Crack Resistance and Stiffness

Another important property of the blend resins of this invention is their outstanding environmental stress crack resistance. Several of the samples are compared with data from polymers of comparable

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melt index and density in Table XVIII produced with a commercially available chromium oxide supported on coprecipitated silica-titania (cogel) catalyst.

TABLE XVIII

COMPARISON OF ESCR DATA FOR BLENDS WITH COMPARABLE COGEL RESINS

	Melt Index (g/10 min)	Density (g/cc)	Flexural Modulus (MPa)	Bell ESCR (hrs)
		0.9500		
Control	0.19	0.9503	1179	530
Control	0.12	0.9503	1172	400
Invention Blend	0.21	0.9500	1255	>1000
		0.9536		
Control	0.24	0.9536	1303	150
Control	0.22	0.9537	1317	115
Invention Blend	0.20	0.9536	1400	>1000
		0.9540		
Control	0.30	0.9543	1372	110
Control	0.20	0.9540	1296	130
Invention Blend	0.12	0.9547	1551	>1000
		0.9570		
Control	0.17	0.9573	1374	326*
Control	0.18	0.9568	1360	326*
Control	0.19	0.9572	1410	338*
Invention Blend	0.18	0.9570	1556	>1000

*These three polymers were made from 1000°F activation temperature catalysts to give maximum ESCR.

Note that in all cases the cogel polymers have ESCR values of only a few hundred hours, while all of the blends have ESCR values of >1000 hours. In fact, not one single specimen failed during the 1000 hours for any of the blends in Table XVIII.

Significantly, the stiffness of these polymers is in every case greater than that of the comparable cogel polymers by approximately 100 MPa. Thus the resins of this invention have achieved the outstanding feat of both superior stiffness and ESCR.

Several of these polymer blends were evaluated in blow molded bottles, where it was noted that they were remarkably uniform and free of streaks. Their color and odor were also excellent. These resins were judged to be superior to typical polyethylene resins in this regard.

Example XII

In this example, 42 blends were prepared from resins within the limits specified above and their physical properties and flow properties were determined. Results are listed in Table XV. Mathematical regression analysis of the results obtained was made to ascertain the significance of the independent variables on blend properties. The following significant dependencies were found:

$$(\text{HLMI})_{\text{Blend}} = 55.67 - 108.33(W_1) + 11.61\ (\text{HLMI}_1) + 0.021\ \text{MI}_2$$

$$(\text{MI})_{\text{Blend}} = 0.8968 - 1.761(W_1) + 0.231(\text{HLMI}_1)$$

$$(\text{Density})_{\text{Blend}} = -0.053 - 0.0393(W_1) + 0.644(D_1) + 0.439(D_2)$$

$$(\text{Dart Impact})_{\text{Blend})} = 2165 - 2063(D_1) - 75.07(\text{HLMI}_1)$$

$$[\text{Spencer(Joules)}]_{\text{Blend}} = 0.5107 - 0.1369(\text{HLMI})_1$$

$$(\text{Elmendorf, MD})_{\text{Blend}} = 2038 + 152.8(W_1) - 1671(D_1 - 9.74(\text{HLMI}_1) - 518(D_2)$$

$$(\text{Elmendorf, TD})_{\text{Blend}} = 5870 + 83.88(W_1) - 6367(D_1) - 106.7(\text{HLMI}_1)$$

W_1 = Weight fraction of high MW component
D_1 = Density of high MW comonent
HLMI_1 = HLMI of high MW component
D_2 = Density of low MW component
MI_2 = MI of low MW component

Conclusions reached from multiple regression analysis:

1. The HLMI and MI of the blend is primarily dependent on weight fractions and HLMI of the high molecular weight component.

2. Density of the blend is primarily dependent on the densities of each of the components.

3. Dart impact of the blend is primarily dependent on the density and HLMI of the high molecular weight component.

4. Spencer impact of the blend is primarily dependent on the HLMI of the high molecular weight component.

5. Elmendorf tear, MD, is dependent on weight fraction, density and HLMI of the high molecular weight component and the density of the low molecular weight component.

6. Elmendorf tear, TD, is dependent on the weight fractions, density and HLMI of the high molecular weight component.

Reasonable variations and modifications can be made in this invention without departing from the spirit and scope thereof.

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Claims

1. Ethylene polymer blend comprising
   (a) 40-70 parts by weight of a high molecular weight ethylene polymer having a high load melt index (HLMI) in the range of 0.1 to 1.5 g/10 min, and
   (b) 60-30 parts by weight of a low molecular weight ethylene polymer having a melt index (MI) in the range of 45-300 g/10 minutes.

2. The blend of claim 1 characterized in that both ethylene polymers (a) and (b) have a narrow molecular weight distribution.

3. The blend of claim 1 or 2 characterized in that said polymer (a) is a polymer of ethylene and 0 to 30 weight percent mono-1-olefin having 3-10 carbon atoms, and said polymer (b) is an ethylene homopolymer.

4. The blend of any of claims 1 to 3 characterized in that neither polymer (a) nor polymer (b) has any substantial long chain branching.

5. The blend of any of claims 1 to 4 characterized in that polymer (a) has a high load melt index (HLMI) in the range of 0.2-0.6, the ethylene homopolymer (b) has a melt index (MI) of 100-300, the ethylene homopolymer (b) is essentially linear and polymer (a) is essentially linear and has essentially only short chain branching from the comonomer, if any.

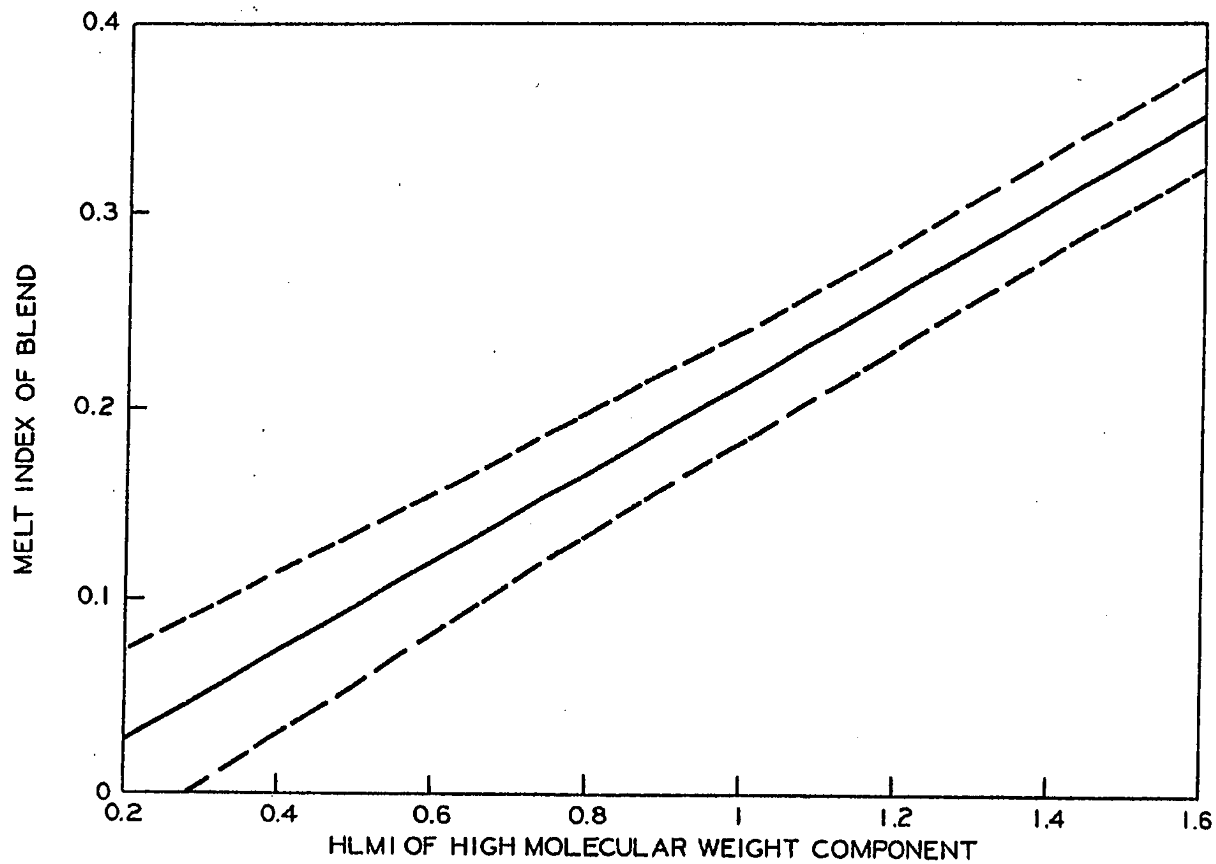
6. The blend of any of claims 1 to 5 characterized in that said high molecular weight ethylene polymer (a) has a density in the range of 0.930 to 0.955 g/ml and said low molecular weight ethylene polymer (b) has a density in the range of 0.945 to 0.975 g/ml.

7. Ethylene polymer blend comprising
   (a) a high molecular weight ethylene polymer randomly copolymerized from ethylene and 5 to 10 weight % of a mono-1-olefin of 4 to 8 carbon atoms, and
   (b) a low molecular weight ethylene homopolymer.

8. A process for producing an ethylene polymer blend characterized by blending 40 to 70 parts by weight of a high molecular weight ethylene polymer (a) according to any of claims 1 to 7, and 60 to 30 parts by weight of a low molecular weight ethylene polymer according to any of claims 1 to 7.

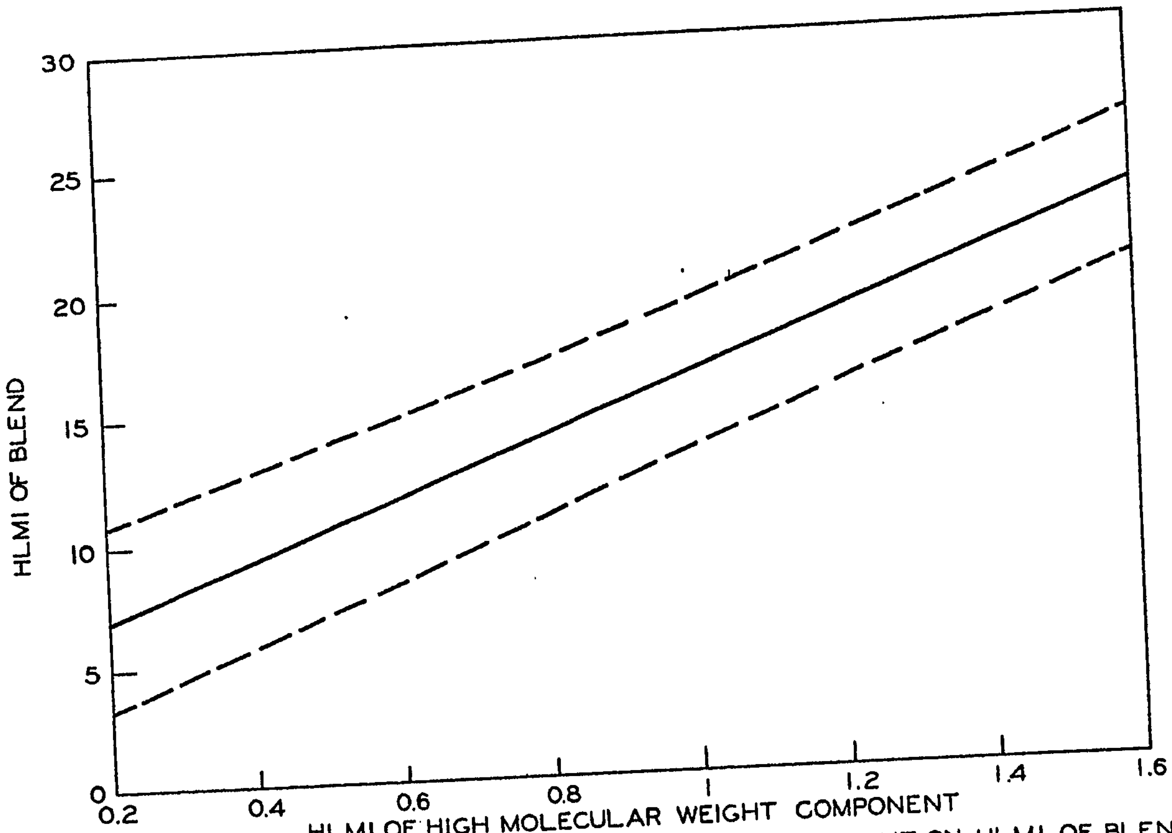
9. The process of claim 8 characterized in that both ethylene polymers (a) and (b) are blended as polymer fluff to obtain a polymer fluff blend as the product.

10. A process for producing an ethylene polymer sheet comprising extruding a fluid ethylene polymer blend and forming the extruded blend into a sheet characterized by using the ethylene polymer blend of one of claims 1 to 7.



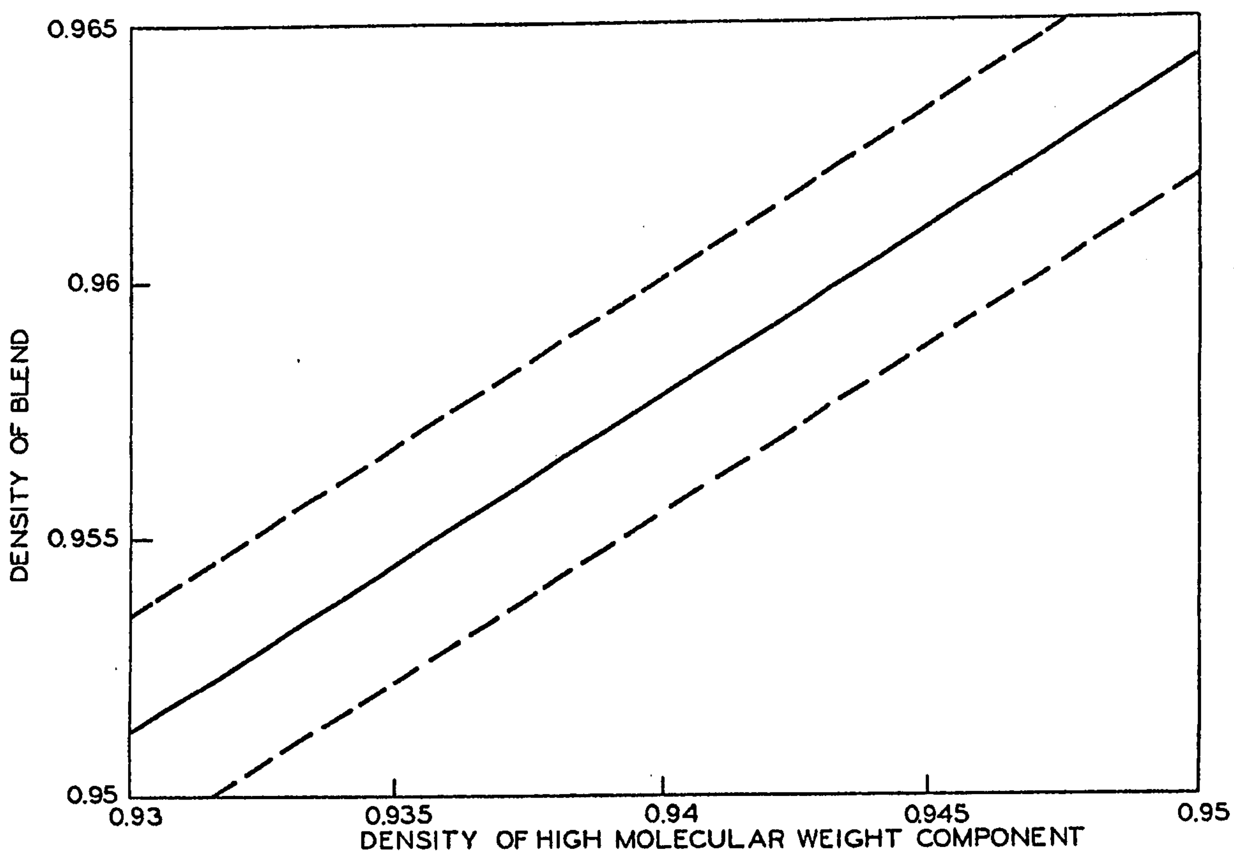
EFFECT OF HLMI OF HIGH MOLECULAR WEIGHT COMPONENT ON MELT INDEX OF BLEND. CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 1



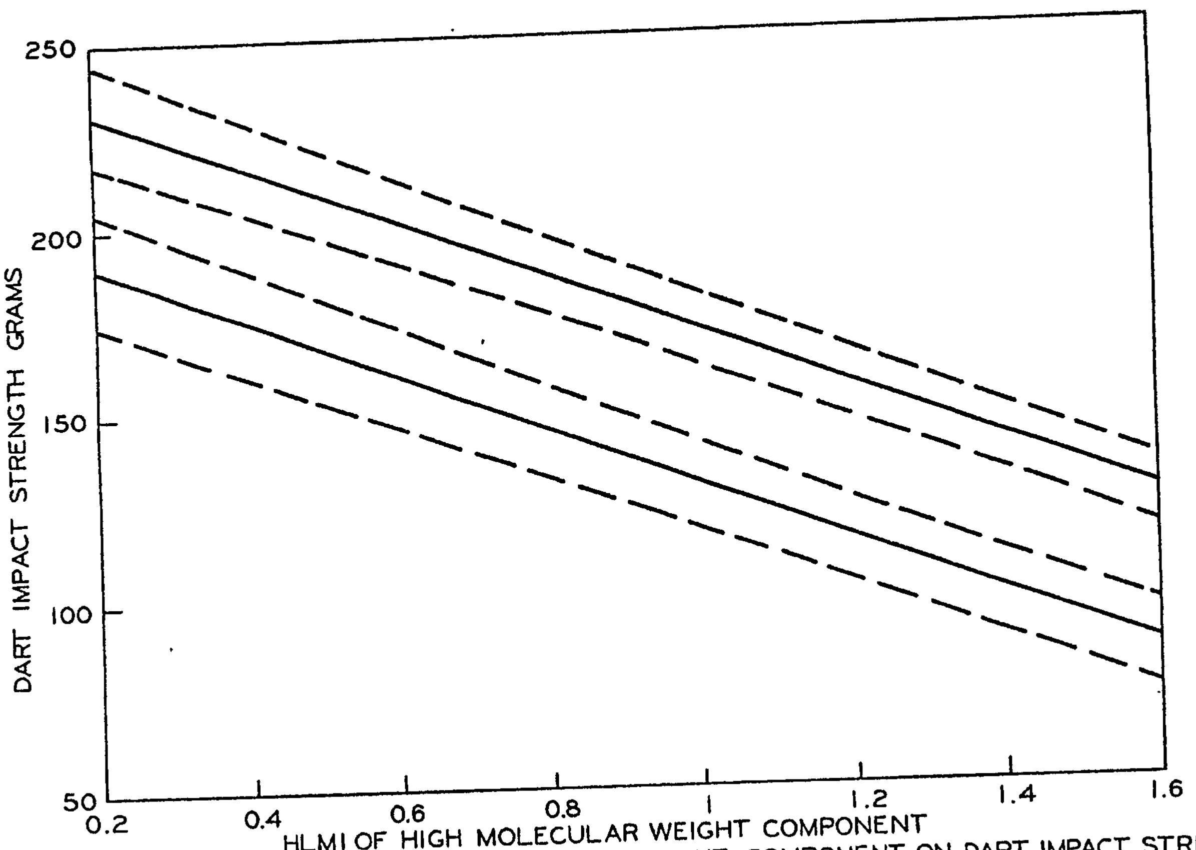
EFFECT OF HLMI OF HIGH MOLECULAR WEIGHT COMPONENT ON HLMI OF BLEND. CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. MELT INDEX OF LOW MOLECULAR WEIGHT POLYMER IS 250. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 2



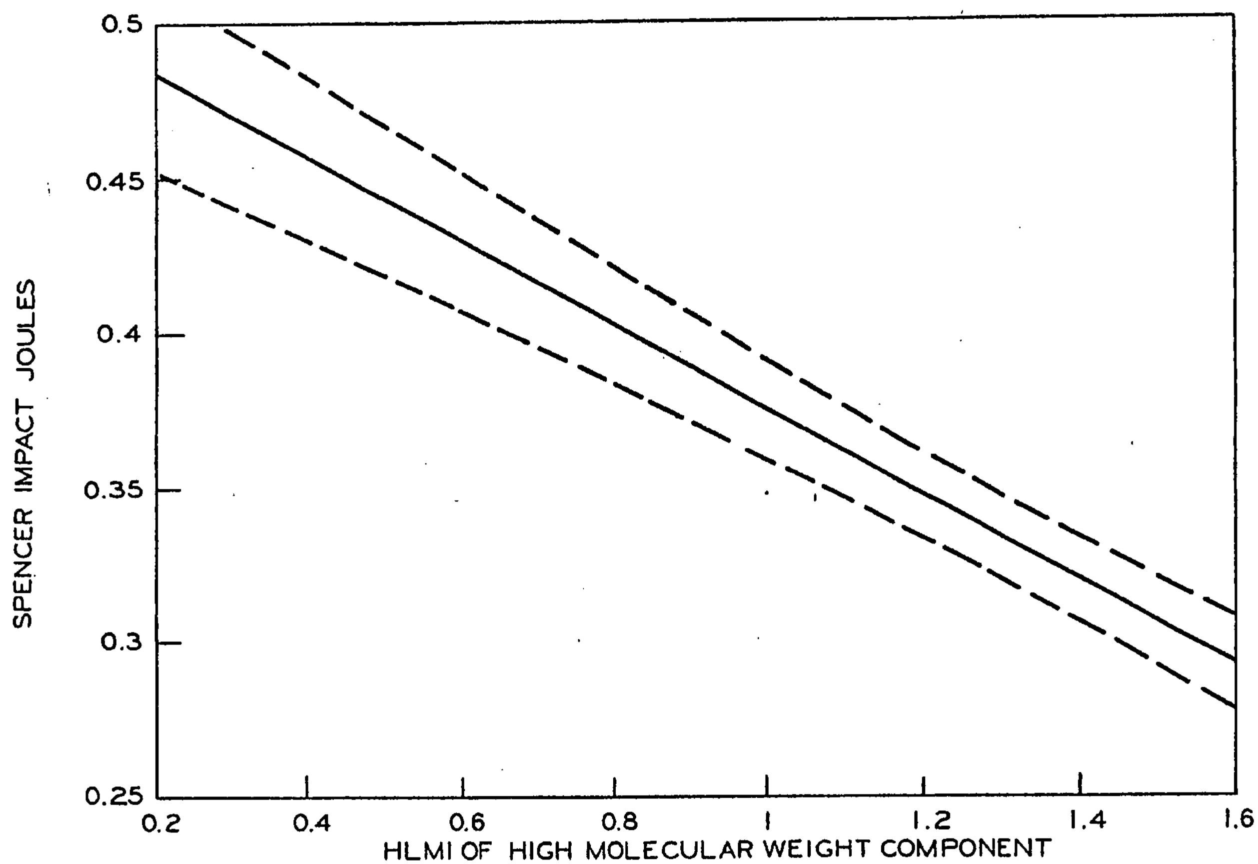
EFFECT OF DENSITY OF HIGH MOLECULAR WEIGHT COMPONENT ON DENSITY OF BLEND CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. DENSITY OF LOW MOLECULAR WEIGHT POLYMERS IS 0.970. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 3



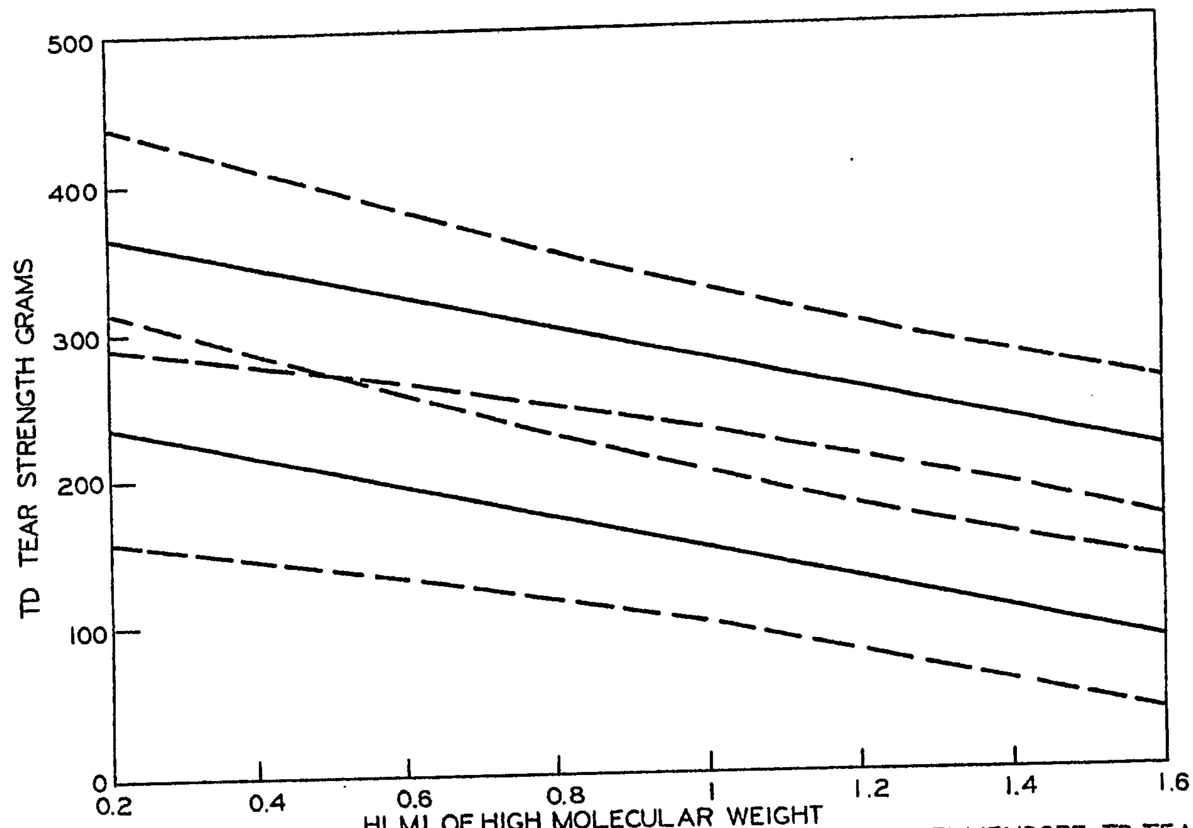
EFFECTS OF HLMI AND DENSITY OF HIGH MOLECULAR WEIGHT COMPONENT ON DART IMPACT STRENGTH OF 1MIL BLOWN FILM(4:1BUR) MADE FROM BLEND. CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. MELT INDEX AND DENSITY OF LOW MOLECULAR WEIGHT POLYMER ARE 250 AND 0.970. DENSITY OF HIGH MOLECULAR WEIGHT POLYMER IS 0.930 FOR UPPER CURVE AND 0.950 FOR LOWER CURVE. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 4



EFFECT OF HLMI OF HIGH MOLECULAR WEIGHT COMPONENT ON SPENCER IMPACT STRENGTH OF 1 MIL BLOWN FILM(4:1 BUR) MADE FROM BLEND. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 5



EFFECT OF HLMI AND DENSITY OF HIGH MOLECULAR WEIGHT COMPONENT ON ELMENDORF TD TEAR STRENGTH OF 1 MIL BLOWN FILM (4:1 BUR) MADE FROM BLEND. CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. MELT INDEX AND DENSITY OF LOW MOLECULAR WEIGHT POLYMER ARE 250 AND 0.970. DENSITY OF HIGH MOLECULAR WEIGHT POLYMER IS 0.930 FOR UPPER CURVE AND 0.950 FOR LOWER CURVE. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

FIG. 6

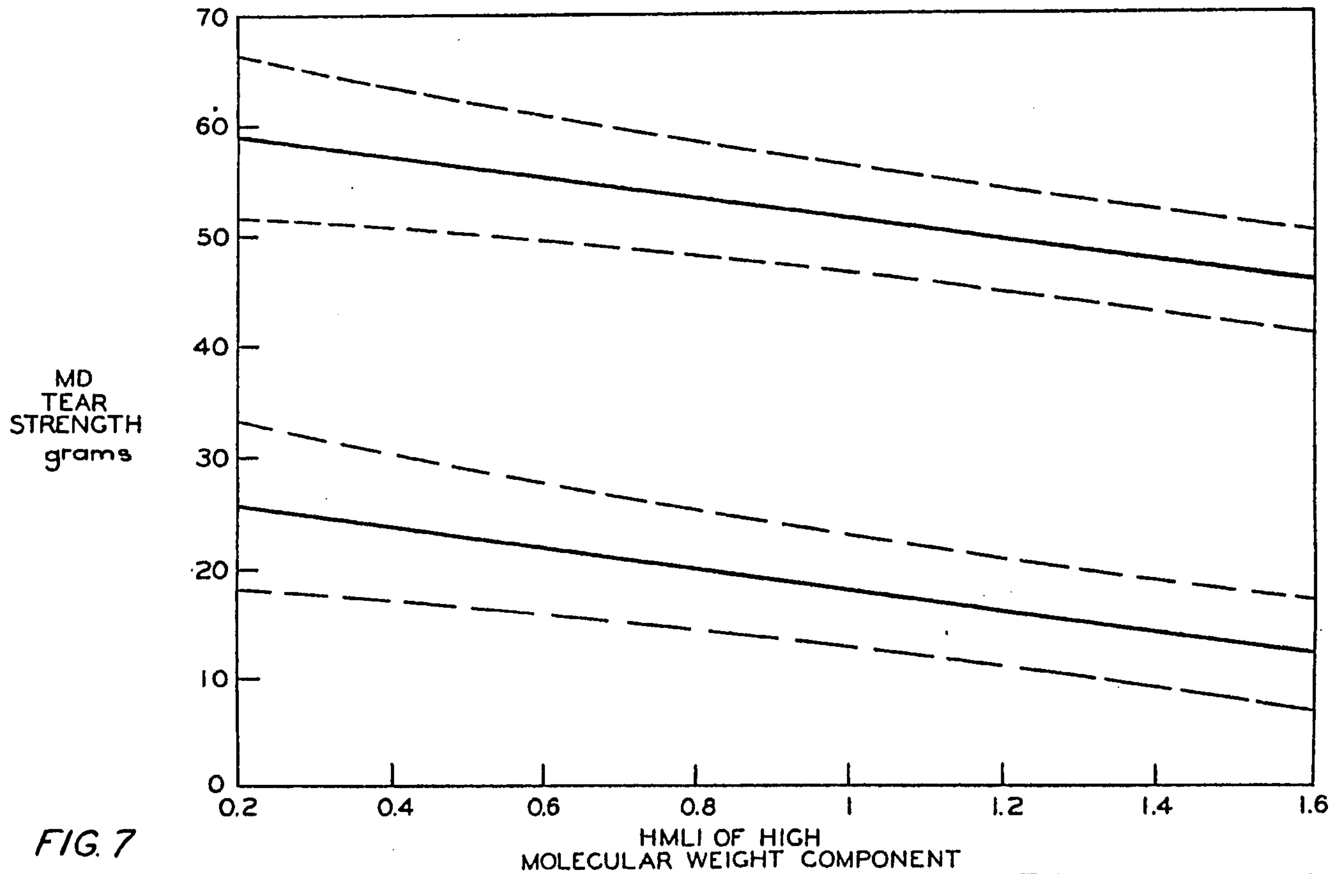


FIG. 7

EFFECT OF HLMI AND DENSITY OF HIGH MOLECULAR WEIGHT COMPONENT ON ELMENDORF MD TEAR STRENGTH OF 1 MIL BLOWN FILM (4:1 BUR) MADE FROM BLEND. CONCENTRATION OF HIGH MOLECULAR WEIGHT POLYMER IS 52%. MELT INDEX AND DENSITY OF LOW MOLECULAR WEIGHT POLYMER ARE 250 AND 0.970. DENSITY OF HIGH MOLECULAR WEIGHT POLYMER IS 0.930 FOR UPPER CURVE AND 0.950 FOR LOWER CURVE. DASHED LINES ARE 95% CONFIDENCE INTERVALS.

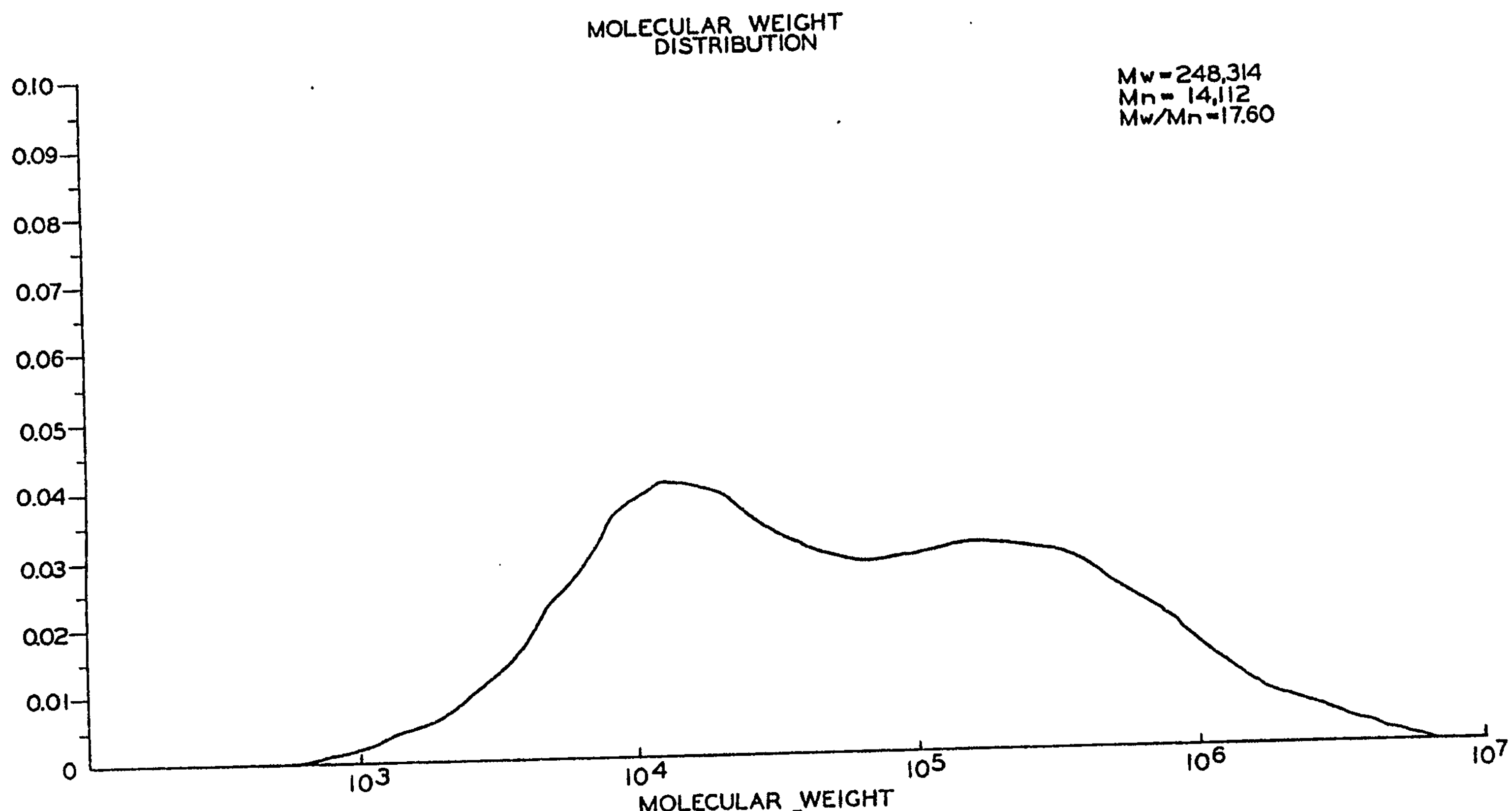


FIG. 8

MOLECULAR WEIGHT DISTRIBUTION CURVE
FOR 50/50 BLEND OF 21L(275 MI)& 2H(0.3HMLI)

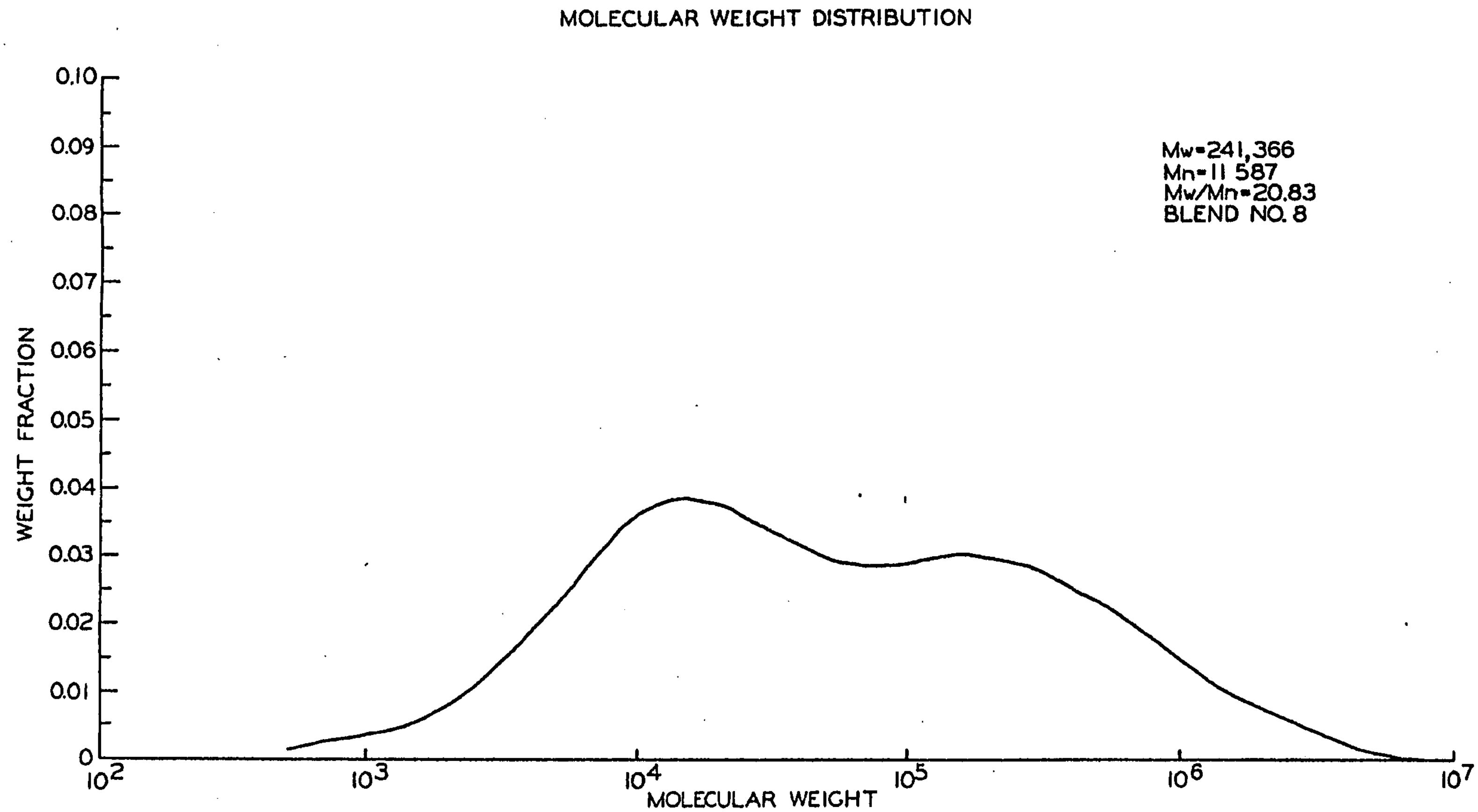


FIG.9

MOLECULAR WEIGHT DISTRIBUTION CURVE FOR 50/50 BLEND OF 23L(212MI) AND 3H(0.37 HLMI).

European Patent Office

EUROPEAN SEARCH REPORT

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Application number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-A-4 230 831 (H. SAKURAI) * Column 1, line 39 - column 4, line 41 * ---	1-10	C 08 L 23/04 C 08 J 5/18
X	US-A-4 123 476 (BONNEFON) * Claim 1 * ---	1	
A	GB-A-2 070 625 (NIPPON OIL) * Claims 1,13 * ---	1,3,10	
A	EP-A-0 005 268 (BASF) * Claim 1 * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

C 08 L
C 08 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03-11-1983	GOOVAERTS R.E.

CATEGORY OF CITED DOCUMENTS

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Y : particularly relevant if combined with another document of the same category
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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